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[Tröpfchenbildung in Dämpfen]

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DROPLET FORMATION IN VAPORS

Max Volmer and Håkon Flood

Droplet formation in adiabatic expansion of vapors was investigated to test the nucleation theory of M. Volmer and L. Farkas. The dependence of the critical supersaturation for water vapor on the temperature is in satisfactory agreement with the theory. The value of the critical supersaturation was determined for 7 organic vapors. Good approximation to the theoretically calculated value was found in 6 cases.

I. Introduction

The object of this work is a comparison of the nucleation theory of M. Volmer[1] and L. Farkas [2] with experience on droplet formation in supersaturated vapors. As is well known, the supersaturated state of vapors can be maintained only briefly and in the presence of a carrier gas. Otherwise there is separation of the liquid and warming of the vapor at the vessel walls. Adiabatic expansion is the usual means for supersaturating a saturated vapor. Droplet formation by this method has often been the object of studies, but almost all of these have been concerned with the condensing effect of external factors such as dust particles, ionization, impurities, etc. As only homogeneous nucleation in a pure vapor can at present be calculated quantitatively according to the theory, most of the older studies are without interest for our problem. It is possible to observe only the degree of expansion (or the supersaturation) at which droplet formation just becomes noticeable (critical degree of expansion or critical

supersaturation). The theory, in comparison, provides the steady number of droplets appearing per second, z , in case the supersaturation is maintained constant. According to the theory, the number, z , increases very rapidly from unmeasurably small values with increasing supersaturation, so that the theoretical sense of critical supersaturation, or the "metastable boundary" is, according to Ostwald, that supersaturation at which the process jumps into appearance.

By a nucleus in a supersaturated phase, we mean, following Volmer, a structure of the new phase which is so large that it is in (labile) equilibrium with the supersaturated phase. In order to produce it, an amount of work

$$W = 4\pi\sigma r^2/3$$

is necessary (σ = surface tension, r = radius of the nucleus). This is primarily decisive for the frequency with which these nuclei are formed through spontaneous fluctuations. Here r depends on the ratio $p_r/p_\infty = S$ (supersaturation according to C. T. R. Wilson) according to the formula of W. Thomson:

$$R T \ln (p_r/p_\infty) = 2\sigma M / r d$$

(p_r = vapor pressure of a droplet with radius r , p_∞ = vapor pressure above a flat surface, M = molecular weight, d = density of the liquid).

According to Farkas, strict performance of the calculation gives

$$z = C \alpha p_\infty \frac{M}{d \cdot N} \sqrt{\frac{\sigma}{kT}} e^{-W/kT} \quad (1)$$

(z = number of droplets appearing per cubic centimeter per second; C = a constant $\sim 10^{-18}$, αp_r = collisions per second per square centimeter; N = Loschmidt number, k = Boltzmann constant).

The critical supersaturation is determined by a nucleus number on the order of 1 per cubic centimeter per second.

Then

$$\log S_{kr} \approx k \left(\frac{q}{T} \right)^{3/2} \left(\frac{M}{d} \right), \quad (2)$$

because the constants for the individual system in the factor before the exponent (Formula 1) are of secondary importance in comparison to it, at least if one is comparing related nucleation processes, such as nucleation in different vapors having vapor pressures of the same order of magnitude.

There are two possibilities for testing the validity of Formulas (1) and (2). First, one can study the temperature dependence of the critical supersaturation. Second, one can compare the specific critical supersaturations of different vapors. Both paths are followed in the present studies. First, we describe experiments on the shift of the metastable boundary of supersaturated water vapor with the temperature. Then we compare some specific critical supersaturations.

The dependence of the droplet number on the supersaturation should offer a third possibility for testing the theory experimentally. Such measurements have been done by Andren [3], among others. They show a smaller rise in the nucleus number with the supersaturation than can be calculated from the theory. But the calculation of the experimental supersaturations is done under the assumption that both the amount of vapor

condensed and the amount of heat liberated in the condensation can be neglected. This would be proper only if the growth rate of the droplets to visible structures was small in comparison with the expansion rate. This is an assumption which is hardly valid, as one can show by a simple calculation. For the same reason, the supersaturations at the so-called fog point, which are very often found in the literature, are of doubtful value.

II. Experimental

1. Calculation of the Supersaturation

With Wilson, one can establish the ratio of the existing vapor pressure to the saturation pressure at the same temperature as a measure of the supersaturation; that is:

$$S = p'/p_{\infty},$$

where p' is the vapor pressure (partial pressure), p_{∞} is the saturation pressure at the same temperature. We shall retain this designation in the following, although the definition of superation according to Volmer and Weber [1] would be more reasonable:

$$U = \ln p'/p_{\infty} \quad \text{or} \quad U = \frac{p' - p_{\infty}}{p_{\infty}}$$

because then we have $U = 0$ for $p' = p_{\infty}$, that is, if there is no supersaturation.

If a volume of gas, v_1 , at temperature T_1 , saturated with a vapor, is adiabatically expanded to the volume v_2 and the temperature T_2 , then supersaturation appears:

$$S = p_1 v_1 T_2 / p_2 v_2 T_1,$$

where p_1 and p_2 are the saturation pressures at the corresponding temperatures.

One can find T_2 from $v_2/v_1 = E$ (E = degree of expansion) by means of the well known adiabatic equation:

$$T_2 = T_1 [v_2/v_1]^{1-\kappa}, \text{ where } \kappa = c_p/c_v.$$

If the gas consists of two components, κ must be calculated additively.

According to F. Richarz [4], one can write

$$\frac{1}{\kappa-1} = \frac{1}{\kappa_1-1} \frac{p_1}{P} + \frac{1}{\kappa_2-1} \frac{p_2}{P}.$$

Here p_1 and p_2 are the partial pressures of the first and second components, P is the total pressure of the mixture ($P = p_1 + p_2$). We can calculate κ from this.

The degree of expansion, $E = v_2/v_1$, is calculated from the measured pressure difference, ΔP , before and after the expansion.

If we assume that the expanded gas volume has again taken on the temperature of the environment at the pressure reading and is saturated with vapor, then

$$v_2/v_1 = P_1/P_2,$$

where P_1 and P_2 are the partial pressures of air in the mixture.

Furthermore, we have

$$P_1 = B - \Delta P' - p_1$$

(B = barometer reading, $\Delta P'$ = pressure difference between the atmospheric pressure and the total pressure of the mixture before expansion, p_1 = saturation pressure of the liquid at the temperature T_1) and

$$P_2 = P_1 - \Delta P.$$

2. Apparatus

An apparatus essentially resembling Wilson's apparatus [5] was used for the measurements. Figure 1 shows the apparatus. A is the expansion cylinder with a volume of some 1,000 cm³.

The expansion cylinder is closed at the bottom by the piston, E, floating in mercury. The expansions are initiated by pulling out the plug B, so that the air space under the piston is connected with the water aspirator vacuum in vessel C (of 5 liters volume). The liquid, the vapor of which is being investigated, is partially in the leveling tube, D, and partly in the expansion cylinder, A. To vary the degree of expansion, one allows some liquid to flow over from the cylinder into the leveling tube, so that the piston, E, is raised and the expansion is increased, without changing the air volume in the expansion volume. The pressure in cylinder A is measured with manometer F before and after the expansion. The mercury is always adjusted to the mark, G, at the right side of the manometer. A small correction must be applied to the pressure difference read to take into account the change in the liquid level over the piston because of the expansion. The level of

mercury in the left leg of the manometer, corresponding to the atmospheric pressure (to determine the $\Delta P''$ value), was established before each series of observations by opening the stopcock H. After the end of the expansion, the piston is placed in the original position by inserting the plug B and allowing air to enter through the pinchclamp I.

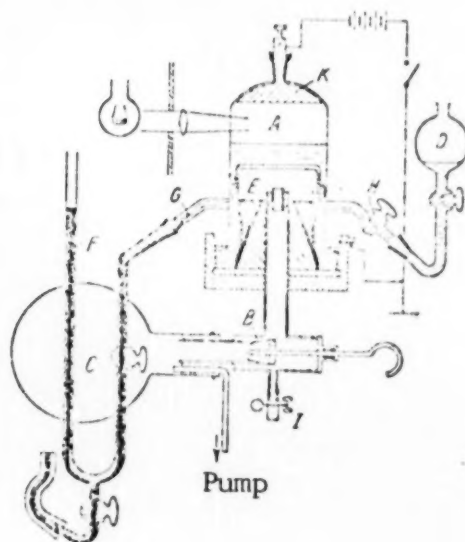


Figure 1.

Drop formation is observed directly above the piston with side lighting from a 500 watt lamp, the heat radiation of which is absorbed in a chilled copper sulfate solution. For experiments in an electrical field, a potential difference of 250 volts was applied between the piston and the electrode, K. Other experimental details, effect of the expansion rate, etc., are reserved for a further report.

Droplet formation begins rather sharply at the so-called critical expansion. If the expansion is increased, the number of droplets forming increases rapidly. But the phenomenon is often not so simple. Splashes or turbulence cause individual droplets to be observable even below the true critical expansion. In these cases, the characterization of the critical degree of expansion which we were seeking is just the fact that a small increase in expansion produces a distinct multiplication of the droplets.

In measurements without application of an electrical field, that is, in the presence of the always-present gas ions, this limit is generally determinable to ± 0.1 cm without difficulty for expansions of about 15 cm, and quite often to ± 0.05 cm. In the presence of an electrical field, there is much more variation in establishment of the limit, as Wilson [6] and Laby [7] have also noted. Here, one must be satisfied with ± 0.1 to ± 0.2 cm. This may perhaps be related to the fact that the gas ions are only incompletely removed by the electrical field if the lines of force do not penetrate the entire gas volume (e. g., leave free the small space behind the electrode). For our problem this situation plays no great part, as we are dealing with a comparison with nucleation theory to establish those expansions which produce the same number of droplets in various vapors. (This droplet number must be as low as possible so that the cooling temperatures from the expansion are not affected by the heat of condensation which develops in droplet formation.)

III. Measurements

1. The Temperature Dependence of the Critical Supersaturation

The objective of these measurements was an orientation on the temperature dependence of the critical supersaturation of water vapor. There are some earlier measurements in the older literature, but these are of a more qualitative measure, and were determined without the presence of an electrical field. Wilson [6] reports having found $E = v_2/v_1$ constant at 1.25 ± 0.01 within the small temperature range from -10° to $+2^\circ$ (cooling temperatures).

Przibram [8], using a special apparatus without a manometer, has found that E has the same value at $+25^\circ$ as at -5° , within a measuring error of 4%.

In the present investigations, the temperature was varied simply by keeping the entire work-room at constant temperature between 12 and 30° . Observations were made alternately at 12 to 16° and at 29 to 32° . The results of the measurements are summarized in Table 1 and plotted in Figure 2, which shows the critical supersaturation as a function of the cooling temperature. The critical degrees of expansion observed without the presence of an electrical field are also listed in Table 1. As one can see, these prove to be rather independent of the temperature, as Wilson and Przibram also found. On the other hand, there is a small but distinct temperature effect in the field.

The cooling temperatures, T_2 , and the critical supersaturations, S_{kr} , have been calculated from the observations in the electrical field. The κ values were found by Richarz's formula, setting $\kappa_{\text{air}} = 1.403$ and $\kappa_{\text{water}} = 1.385$.

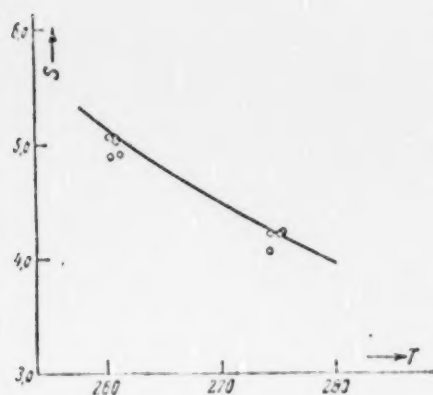


Figure 2.

Table 1:

	T_1	$\overbrace{E}^{\text{without F}}$		ν	T_2	S_{kr}
		without F	with F			
1	303.0	1'250 ₁	1'269 ₁	1'402 ₂	275.3	4.22
2	302.8	1'249 ₂	1'268 ₂	1'402 ₂	275.2	4.21
3	300.0	1'247 ₃	1'258 ₃	1'402 ₂	274.3	4.06
4	301.7	---	1'267 ₄	1'402 ₂	274.3	4.21
5	288.3	1'248 ₅	1'275 ₅	1'402 ₂	261.4	4.91
6	288.2	---	1'279 ₆	1'402 ₂	261.0	5.04
7	288.1	1'248 ₇	1'278 ₇	1'402 ₂	261.0	5.02
8	287.1	1'246 ₈	1'273 ₈	1'402 ₂	260.5	4.89
9	287.5	1'249 ₉	1'278 ₉	1'402 ₂	260.4	5.00

These values can be compared directly with those calculated by means of the theoretical formula (2). The empirical constant d has been determined from the value for water vapor, $S = 4.85$ at $T_2 = 264$ ($k = 0.242$). The surface tensions at the temperatures involved have been determined through graphical extrapolation of the tabulated values. The critical supersaturations calculated from the theory in this manner are plotted as the solid curve in Figure 2.

As one can see, there is a quite satisfactory agreement between theory and experiment, to the extent that we may make a conclusion from the small temperature interval.

2. The Critical Supersaturation for Some Organic Liquids

There has been previous work on droplet formation in organic vapors, even in connection with studies of air electricity. Przibram [9] measured a series of vapors, especially alcohols, with artificial ionization from a radium preparation. He investigated the difference of the condensing effect of positive and negative ions. But it appears that his apparatus did not provide completely adiabatic expansions, as he found $S_{kr} = 4.4$ for water vapor in spite of the artificial ionization, while other authors obtained 3.6 to 4.0 under the same conditions. Laby [10] has measured some esters and acids with and without ionization from X-rays. For water vapor without ionization he found $S_{kr} = 4.2$ (Wilson 4.1).

The value found by Donnan [11] for water vapor is much too high ($S_{kr} = 5.0$). His other results which can be checked also indicate that his apparatus did not operate adiabatically.

Andren [12] measured ethyl alcohol and benzene vapor, and also measured the alcohol vapor in an electrical field. His results were cited elsewhere.

Finally, various organic materials and their mixtures were investigated by Bayerl-Bröse [13].

In this work, we studied the following materials:
 H_2O , CH_3OH , C_2H_5OH , $n-C_3H_7OH$, $iso-C_3H_7OH$, $n-C_4H_9OH$, CH_3NO_2
and $CH_3COOC_2H_5$.

Very few materials are suited for the study. First, the partial pressure of the vapor in the air-vapor mixture must be low if x_{vapor} is not known with adequate certainty (x_{mixture} must also not be too low). Second, the vapor must give droplet formation at not too great expansions, as otherwise the expansions must be considered non-adiabatic. For our apparatus the upper limit may be about $E \sim 140$. This condition excludes most liquids which do not have relatively low molar volumes (M/d). Therefore, suitable liquids for the measurements should be sought among those which have relatively low molar volumes and are also not very volatile. These conditions are usually mutually exclusive.

Furthermore, the liquids must be chemically indifferent toward the parts of the apparatus and must be stable, so that they can be purified sufficiently.

The liquids measured were all carefully purified. Methyl and ethyl alcohol were distilled over CaO , while steam was passed through to remove aldehydes. Propyl, isopropyl and butyl alcohol (Kahlbaum, highest purity) were also distilled over CaO . Nitromethane was washed with salt water, dried with P_2O_5 , and distilled. Ethyl acetate (D. A. B. 6) was repeatedly extracted with salt-saturated water, dried several times with fresh CaCl_2 , and distilled.

Each substance was measured several times. The $\pm$ limits shown in the following Table 2 are the error limits for a single establishment of the critical supersaturation. The actual error limits, then, could be somewhat greater. The data of Table 2 represent the most probable values from our observations. Averaging of the individual observations is not very reasonable because the cooling temperatures are not

Table 2

Material	T_1	E		α_1	α_2	T_2	S_{kr}
		* P	** P				
Water	291	1'251	1'276	1'385	1'403	263'7	4'85 $\pm$ 0'08
Methyl alcohol	295	1'257	1'285	1'203	1'353	270'0	3'20 $\pm$ 0'1
Ethyl alcohol	289'5	1'152	1'172	1'13	1'364	273'2	2'31 $\pm$ 0'05
n-Propyl alcohol	289	1'172	1'190	(1'11)	1'387	270'4	3'05 $\pm$ 0'05
Isopropyl alcohol	283'2	1'177	1'190	(1'11)	1'381	261'7	2'80 $\pm$ 0'07
n-Butyl alcohol	291	1'190	1'206	(1'09)	1'397	270'2	4'60 $\pm$ 0'13
Nitromethane	291'5	1'425	1'402	(1'15)	1'380	252'2	6'03 $\pm$ 0'15
Ethyl acetate	290	1'620	1'715	(1'13)	1'343	240	12'3
		1'575	1'670	(1'13)		244	8'0

*without **with

exactly the same. With ethyl acetate, however, the values fluctuate considerably, and two extreme values are listed in the table for this material. We did not establish the critical supersaturation more accurately here because the expansions were probably too great to be able to perform an accurate evaluation. Ethyl acetate is also very easily contaminated by its hydrolysis products.

T_1 and T_2 are the temperatures before and after the expansion. E is the critical degree of expansion without, and in the presence of, the electrical field. Column 5 contains the values of $\alpha_1 = C_p/C_v$ for the pure vapor. There are values in the literature only for the first three materials in the table. For the other five, α_1 has been estimated from the data for related materials (values in parentheses). This could give significant uncertainty only in the case of

ethyl acetate. The value of x_2 for the air-vapor mixture is calculated from the x_1 values along with $x_{\text{air}} = 1.403$. The saturation pressures at temperature T_2 are obtained through extrapolation of the pressures at higher temperatures.

There are two determinations of the critical supersaturation of water vapor in the electrical field in the older literature. Wilson reports the value 4.8 at $T = 265$, while Andren finds 5.0 (without stating the temperature). Andren has also measured ethyl alcohol in the field, with the result $S_{kr} = 2.25$.

Table 3

Material	T	M	d	σ	S_{kr}	
					Theor.	Experm.
Water	264	18.0	1.00	77.0	(4.85)	4.85
Methyl alcohol	270	32.0	0.81	21.8	1.84	3.20
Ethyl alcohol	273	46.0	0.81	24.0	2.30	2.31
n-Propyl alcohol	270	60.1	0.82	23.4	3.20	3.05
Isopropyl alcohol	265	60.1	0.81	23.1	2.90	2.80
Butyl alcohol	270	74.1	0.83	26.1	4.50	4.60
Nitromethane	252	61.0	1.20	40.0	6.25	6.05
Ethyl acetate	240	88.1	0.94	30.8	11.0	12.3
	244			30.4	9.8	8.0

The values presented in Table 2 can be used directly to test the theory. This is done in Table 3, in which the experimentally determined critical supersaturations are compared with the values calculated from Formula (2). As before, the empirical constant, k , has been calculated from the data for water vapor. The densities and surface tensions which enter into the calculation are also listed in Table 3. These are extrapolated to the appropriate temperatures.

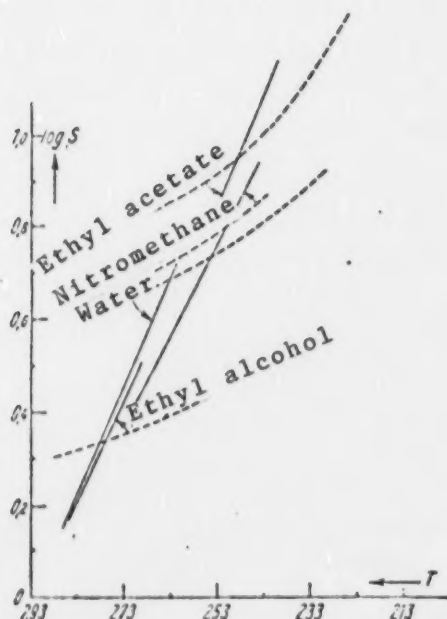


Figure 3.

As appears from Table 3, there is quite good agreement between the experimentally determined and theoretically calculated results for seven of the materials measured. On the other hand, a significant discrepancy appears for methyl alcohol. The theoretical value can hardly contain uncertain factors of significant importance. Possibly an incorrect $\kappa_{\text{methyl alcohol}}$ could have been used in calculating the experimental value. Here, we made the calculation with the value of 1.203, determined by Dixon-Greenwood [14] from sound velocity measurements. The κ values for the other materials also are derived from sound velocity measurements, but for these materials κ is less important because of their lower volatility. Another possible explanation for the discrepancy would be that the supersaturated methyl alcohol vapor is partially associated at the cooling temperature.

To be sure, such behavior does not appear from the vapor density measurements of Young [15], but his measuring accuracy is not very great at his lowest temperature (273°), as he himself says. Thus the explanation of this point requires a special study which is still lacking.

We get an instructive picture of the relation between the supersaturations produced by adiabatic expansion and the critical supersaturations calculated from the theory if we plot both in the same diagram as functions of the cooling temperature. This is done in Figure 3.

The dashed curves are the critical supersaturations calculated according to the formula

$$\log S_{kr} = k \cdot (\sigma/T)^{1/2} \cdot (M/d),$$

in which we assume σ to be a linear function of temperature. The almost linear solid curves going out from $T = T_A = 293^\circ$ are obtained from the formula which had been used earlier:

$$S = p_1 v_1 T / p_2 v_2 T_A$$

(T = cooling temperature, T_A = initial temperature). For this case it takes on a clearer form if one introduces

$$\log \frac{p_1}{p_2} = \frac{Q}{4.57} \frac{T_A - T}{T \cdot T_A}$$

and

$$v_1/v_2 = (T_A/T)^{1-\alpha}$$

Then it becomes

$$\log S = \frac{Q}{4.57} \frac{T_A - T}{T_A \cdot T} - \frac{\kappa}{z - 1} \log \frac{T_A}{T}.$$

The intersections of the two curves for S and S_{kr} represent the critical supersaturations to be expected, or the critical cooling temperatures.

As one can see, the prerequisite for a rapid rise in $\log S$ with the cooling temperature is that Q and κ have the highest possible values. On the other hand, the supersaturation necessary according to the theory for droplet formation is smaller, the smaller the expression $(\sigma/T)^{2/3} \cdot (M/d)$ is. If both these conditions are not met within certain limits, the two curves do not intersect at all, and droplet condensation cannot be expected even at arbitrarily high expansions. As the two conditions are usually mutually exclusive, we can understand that only a few vapors are brought to the point of droplet formation by moderate expansions. (The selection of materials suitable for this study is reduced by the fact that the existing information on measured constants is incomplete.)

As the slope of the $\log S_{kr}$ curve in any case increases faster as the temperature decreases than does that of the $\log S$ curve, then in principle the curves must intersect once. This means that the number of nuclei passes through a maximum as the undercooling increases, falling off again toward zero at still lower temperatures.

This result of the theory applies not only to supersaturated vapors, but quite generally for any nucleation process, as has been shown by Stranski [16].

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